TUNABLE OPTICAL SOURCES

Final Report

for

U.S. Army Research Office (Durham)

Contract No. DAHC-04-68-C-0048

Sponsored by

Advanced Research Projects Agency

ARPA Order No. 675, Am 7

Program Code No. 9E20

for the period

28 June, 1968 – 30 June 1972

M.L. Report No. 2077

July 1972

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on

U.S. Army Research Office (Durham)

Contract No. DAHC-04-68-C-0048

28 June, 1968 – 30 June 1972

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I. RESEARCH OBJECTIVES

The purpose of this contract has been the study of new techniques and devices for obtaining tunable radiation across wide regions of the electromagnetic spectrum. Progress during the contract period has been outstanding. Principal accomplishments include: the construction and demonstration of the first optical parametric oscillator operating in the 9μ to 11μ spectral region; and the proposal and demonstration of the first nonlinear optical technique for access to the vacuum ultraviolet. A brief technical summary of these projects and also of the iodine laser project is given in the following.

II. TECHNICAL SUMMARY

A. CdSe INFRARED PARAMETRIC OSCILLATOR

The preliminary measurements verifying the gain, phase matching, and quality of CdSe have been published in a paper titled "Efficient Parametric Mixing in CdSe". A reprint of this paper is included as an appendix to this report.

We have carried out measurements of threshold, conversion efficiency, bandwidth, and damage threshold of the CdSe infrared parametric oscillator. The principal results were presented in an invited paper at the Montreal Quantum Electronics Conference. They also appear in a preprint of a paper titled "Singly Resonant CdSe Infrared Parametric Oscillator", which is also included as an appendix.

The important results of the study to date are that CdSe crystals are available in high quality up to 3.6 cm in length, the calculated and measured oscillator threshold agree, the resonant signal wave at 2.2μ does cause crystal surface damage due to its high resonant intensity, and resonating the idler wave at 9.6μ to 10.6μ eliminates the damage problem due to the reduced power density at the idler frequency. These results are more fully discussed in the reprint describing the CdSe oscillator.

At this time we have received a new 3.6 cm long CdSe crystal. The crystal has been polished and antireflection coated at 10μ for use in an oscillator. This crystal has less than 0.01 cm^{-1} absorption loss which

is comparable to the best loss reported for CdTe . We expect the reduced loss to allow considerably higher average power operation of the CdSe oscillator.

Resonating the idler wave at 10μ involves considerable expense for infrared optics. We have used GaAs mirrors in the past but find the lack of visible transmission and the very high index of refraction to be disadvantageous. We have therefore spent some effort testing possible mirror substrate materials including germanium, CdTe, CdSe, CdS, silicon, and GaAs . We have also considered various salts. Of these, CdS appears to offer the most advantages at the least cost. Therefore, we have ordered CdS mirror substrates. The substrates will be polished at Stanford and properly coated at a nearby laser company. The coating is expected to cover the 9.6μ to 12μ region with 99% reflectance.

We have angle tuned CdSe from 9.6μ to 10.4μ before being limited by crystal geometry. We expect to extend the tuning range by two means: first, by using a 75° cut crystal so that angle tuning is possible from 90° to 60° which gives the full 9.6μ to 15μ ; and second, by pumping a 90° cut crystal with a tunable pump source. An appropriate tunable pump is the $LiNbO_3$ parametric oscillator pumped with 1.32μ Nd:YAG laser. This oscillator pumped CdSe oscillator would give 0.9μ to 3μ output from $LiNbO_3$ and 1.8μ to 4μ and 8μ to 15μ output from CdSe . Such a source would be of considerable value for many spectroscopic experiments in the infrared.

B. PHASE MATCHED THIRD HARMONIC GENERATION IN METALLIC VAPORS

Present nonlinear optical crystals either become opaque or are not phase matchable for wavelengths shorter than about 2500 Å . To extend

laser techniques into the vacuum ultraviolet and perhaps soft x-ray region of the electromagnetic spectrum we have proposed a technique of phase matched third harmonic generation and frequency summing in mixtures of metallic vapors and inert gases. Metallic vapors are particularly appropriate for nonlinear optical processes of this type due to: first, their very large nonlinearities which result from frequency resonances interspaced in the spectral region of interest; and second, as a result of the fact that in many cases they are negatively dispersive. The key proposal is to make use of the negatively dispersive metallic vapor mixed with a normally or positively dispersive inert gas in a ratio to obtain phase matching over reasonably long cell lengths. During the previous contract period this idea was proposed and a first experimental demonstration of tripling of 1.064μ in a mixture of rubidium and xenon was undertaken. In more recent work we have carried out detailed quantum mechanical calculations of the nonlinear susceptibilities and of saturation processes which are inherent in this process. Most recently, generation of vacuum ultraviolet radiation at 1773 Å , 1520 Å , and 1182 Å has been demonstrated.

We note that the work on this project is jointly supported by contracts with NASA, with the Office of Naval Research, and with the Air Force Cambridge Research Laboratories.

C. OPTICALLY PUMPED MOLECULAR I_2 LASER

We have completed initial analysis of the optically pumped I_2 laser. The results have recently been published and are included in

the appendix. The I_2 molecular laser was also presented at the Quantum Electronics Conference.

The I_2 molecular laser is of considerable interest to spectroscopists and to laser frequency stabilization workers. We believe that the technique of optically pumping molecules will be extended to other systems in the infrared, visible, and ultraviolet. Indeed, extensions of optical pumped molecules to the far infrared, and to the CO_2 molecule have recently been reported.

Work on I_2 may be extended at this laboratory to other molecules. In particular, we are interested in using the CdSe oscillator in the 9.6μ to 15μ region as a pumping source for infrared molecules.

III. LIST OF ALL PUBLICATIONS AND REPORTS PUBLISHED

1. R. L. Byer, S. E. Harris, D. J. Kuizenga, J. F. Young, and R. S. Feigelson, "Nonlinear Optical Properties of $Ba_2NaNb_5O_{15}$ in the Tetragonal Phase," J. Appl. Phys. 40, 444 (January 1969).

2. R. L. Byer and J. F. Young, "Quality Testing of $LiNbO_3$ Crystals," Microwave Laboratory Report No. 1749, Stanford University, Stanford, California (April 1969).

3. R. W. Wallace and S. E. Harris, "Oscillation and Doubling of the .946μ Line in Nd^{3+}:YAG," Appl. Phys. Letters 15, 111 (August 1969).

4. R. L. Byer, J. F. Young, and R. S. Feigelson, "Growth of High-Quality $LiNbO_3$ Crystals From a Congruent Melt," J. Appl. Phys. 41, 2320 (May 1970).

5. R. L. Byer, "Recent Advances in Nonlinear Optical Materials," Optical Spectra, p. 42 (September 1970).

6. R. L. Byer and R. I. Herbst, "Constant Dispersion Rotating Grating Q-Switch," Appl. Optics 9, 2808 (December 1970).

7. S. E. Harris and R. B. Miles, "Proposed Third Harmonic Generation in Phase-Matched Metal Vapors," Appl. Phys. Letters 19, 385 (November 1971).

8. R. L. Herbst and R. L. Byer, "Efficient Parametric Mixing in CdSe," Appl. Phys. Letters 19, 527 (December 1971).

9. R. L. Herbst and R. L. Byer, "Singly Resonant CdSe Infrared Parametric Oscillator," Appl. Phys. Letters (to be published).

IV. LIST OF PARTICIPATING SCIENTIFIC PERSONNEL

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R. B. Miles (Ph.D. obtained June 1972)

APPENDIX A

"EFFICIENT PARAMETRIC MIXING IN CdSe"

Appl. Phys. Letters 19, 527 (December 1971)

APPLIED PHYSICS LETTERS VOLUME 19, NUMBER 12 15 DECEMBER 1971

Efficient Parametric Mixing in CdSe†

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(Received 25 August 1971)

We have obtained the first phase-matched nonlinear interaction in CdSe and have observed a 35% conversion efficiency for mixing 10.6 μ with a pump at 1.833 μ to generate a signal at 2.2 μ. The mixing process phase matches at 77° to the optic axis and confirms the predicted phase-matching angle. The measured nonlinear coefficient value of 2.5×10^{-22} mks agrees with previous results. The mixing experiment shows that an angle-tuned or pump-tuned infrared parametric oscillator is possible using CdSe as the nonlinear element.

CdSe has been proposed as a potential nonlinear material in the infrared spectral region.[1] Its nonlinear coefficient has been previously measured[2] and recently remeasured.[3] However, the previous index-of-refraction and birefringence data[4,5] did not allow phase-matching curves to be predicted. We have remeasured the refractive index of CdSe and have verified that it phase matches over an extended region in the infrared.

CdSe has a wurtzite structure with 6 *mm* point-group symmetry. The components of nonlinear polarization are

$$\begin{aligned} P_x &= 2d_{15}E_zE_x, \\ P_y &= 2d_{15}E_zE_y, \\ P_z &= d_{31}E_x^2 + d_{31}E_y^2 + d_{33}E_z^2, \end{aligned} \tag{1}$$

where $d_{31}=d_{15}$ by Kleinman's symmetry. For a positive birefringent crystal only type-II phase matching is allowed with

$$\omega_3 = \omega_2 + \omega_1$$

and

$$n_3^0\omega_3 = n_2^e\omega_2 + n_1^0\omega_1. \tag{2}$$

Figure 1(a) shows the transmittance of as-grown CdSe and selenium-compensated CdSe. The material grows selenium deficient and must be compensated following growth to obtain semi-insulating crystals with resistivities of $10^6\ \Omega$ cm.[6,7] When properly compensated the transparency extends to 25 μ, where it is limited by two-phonon absorption. We compensated as-grown CdSe crystals by heating the crystals in a 2-atm selenium vapor for two weeks. Compen-

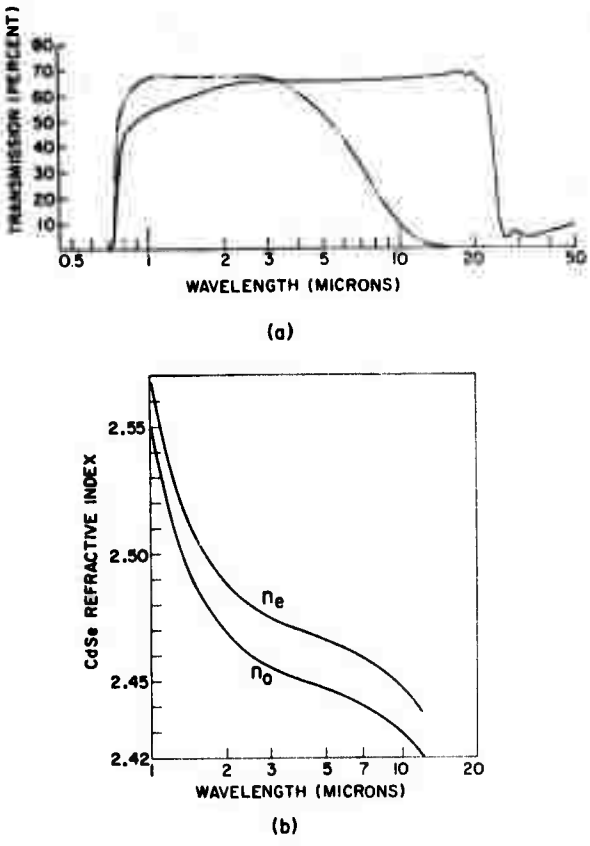

FIG. 1. (a) Transmittance of CdSe; dotted curve for as-grown crystals, solid curve for selenium-compensated crystals. (b) Index of refraction of CdSe.

sated crystals from Gould and Materials Research Corp. showed the expected improved transparency.

Although other nonlinear crystals have a higher figure of merit for nonlinear applications in the infrared than CdSe,[3,8,9] few of these materials have the high optical quality necessary for device construction. To accurately determine the optical quality of CdSe we measured the absorption coefficient at 10.6 μ using a calorimetric technique.[10] From previous theoretical considerations we expect the absorption to be similar to the values measured for high-resistivity GaAs of 0.02 cm^{-1}.[11] The measured absorption for CdSe is 0.032 cm^{-1} which compares favorably with the GaAs value. In addition, the measured value for CdS is 0.026 cm^{-1} and for Ag_3AsS_3 (proustite) is 1 cm^{-1} at 10.6 μ.

Figure 1(b) shows a plot of the CdSe indices of refraction vs wavelength in the transparent region. Table I lists the measured values. The data are taken using the prism technique and a reflecting-optics index-of-refraction table similar to that described by Bond.[4] Diffraction due to the prism's size limits the accuracy of the index measurement to parts in the fourth decimal place.

We fit the index-of-refraction values with a double-pole Sellmeier equation to obtain an analytical expression for $n_0(\lambda)$ and $n_e(\lambda)$. These expressions are then used with the phase-matching condition given by Eq. (2) to calculate tuning curves. CdSe is positive birefringent with enough birefringence to allow off-degeneracy phase matching. However, the birefringence is insufficient to allow phase-matched second-harmonic generation.

Figure 2(a) shows the tuning curve for an angle-tuned parametric oscillator pumped with the 1.833-μ line of a Nd:YAG laser.[12] Also shown is the parametric-gain bandwidth for a 1-cm-long crystal.[13] Figure 2(b) shows a tuning curve for collinear phase-matched CdSe pumped with a tunable pump source. In this configuration CdSe is an infrared frequency converter with output wavelengths in the 2–4-μ and 8–12-μ regions for pump wavelengths between 1.5 and 3 μ.

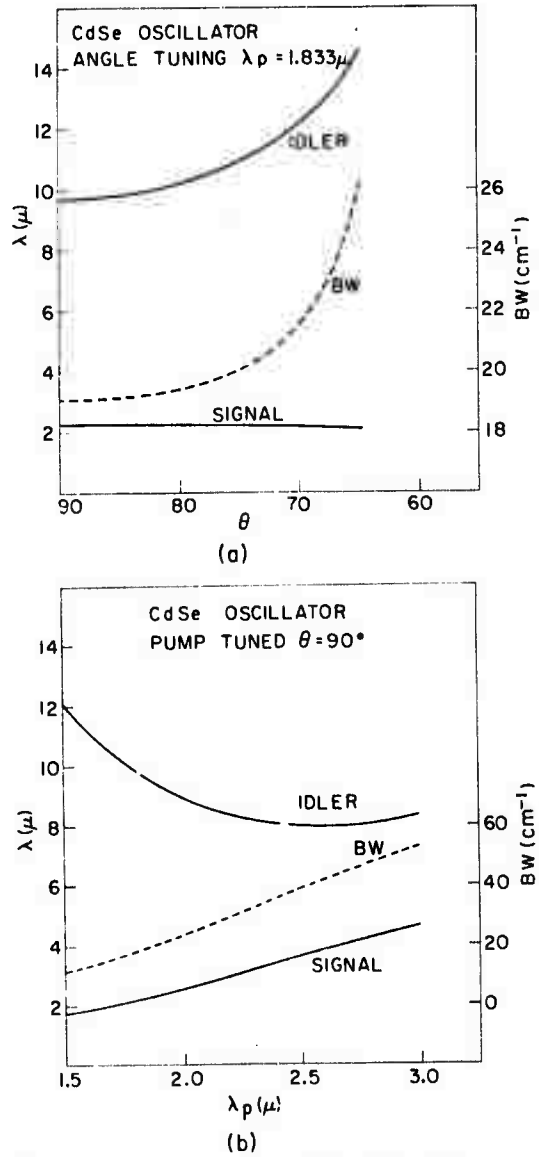

FIG. 2. (a) Angle-tuned CdSe parametric oscillator pumped with 1.833 μ. (b) Collinear phase-matched pumped-tuned CdSe frequency converter.

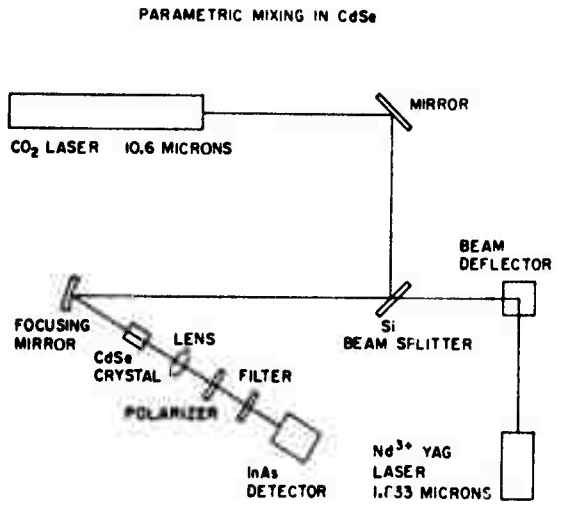

FIG. 3. Schematic of parametric mixing experiment.

A potential pump source is a $LiNbO_3$ parametric oscillator.[14]

Although CdSe has high transparency and optical quality, it is useful to measure its nonlinear properties prior to attempting the construction of a parametric oscillator. Second-harmonic generation (SHG) is not possible, so that the measurement of the nonlinear coefficient and birefringence uniformity by (SHG) cannot be applied.[15] However, mixing[5,16-18] of the CO_2 wavelength at 10.6 μ with 1.833 μ to generate 2.2 μ phase matches at 77° according to Fig. 2(a).

Figure 3 shows a schematic of the mixing experiment. The pump laser is a Q-switched Nd:YAG laser operating at 1.833 μ with up to 2-kW peak power in a 200-nsec pulse The CO_2 laser is a 1-W cw laser with feedback control providing amplitude stability. An InAs detector detects the generated signal at 2.2 μ following a polarizer and filter. A motor-driven stage rotates the CdSe crystal so that the phase-matching angle and $\sin^2(\Delta kl/2)$ signature can be accurately plotted.

The power generated by parametric mixing for a crystal of length l is

$$P_2(l) = P_1(\omega_2/\omega_1)\sinh^2(\Gamma l), \tag{3}$$

where P_1 is the input power and Γ is the gain parameter given by

$$\Gamma = (2\eta_1\eta_2\eta_3\omega_1\omega_2 d_{31}^2 P_3/A)^{1/2}, \tag{4}$$

where η is the impedance, d_{31} is the nonlinear coefficient, and P_3 is the pump power. For a conversion efficiency of less than 50%, $\sinh(\Gamma l) \approx \Gamma l$ so that Eq. (3) reduces to

$$P_2(l) = 2\eta_1\eta_2\eta_3\omega_2^2 d_{31}^2\, P_1P_3/\pi(w_1^2+w_3^2)l^2\,\mathrm{sinc}^2\,\Delta kl/2, \tag{5}$$

where we include the momentum mismatch factor and $A = \pi(w_1^2+w_3^2)$ for Guassian beams. Here we assume that focusing is such that the crystal length and not the aperature length $l_a = \sqrt{\pi w_3}/\rho$ limits the interaction.[19] For the present case we calculate $l_a = 2.64$ cm, which is greater than the crystal lengths of 0.6 −1.0 cm.

Equation (5) shows that d_{31}^2 can be determined if the ratio $P_2(l)/P_3$ and the average power P_1 are known. Experimentally the measurement is straightforward and leads to an accurate value for d_{31}.

In the present experiment we use a 0.6-cm-long crystal of CdSe. A single detector measures the ratio of 2.2-μ power to 1.833-μ power using calibrated filters. The CO_2 laser operates cw at a level near 1 W as measured with a CRL power meter. Using the experimental values and Eq. (5) we find that

$$d_{31} = 2.5\times10^{-22} \pm 15\%.$$

Unlike a previous measurement of d_{31} for CdSe, this value is measured directly and not relative to GaAs.[3]

For the 0.6-cm crystal and focusing such that $\pi w_3^2 = 8.4\times10^{-5}$ cm^2 and $\pi w_1^2 = 6.4\times10^{-4}$ cm^2, a pump power of 2 kW corresponds to an incident power density of 24 MW/cm^2. At this power density the measured mixing efficiency is 35%. Surface damage for CdSe occurs at a power density of 30 MW/cm^2. Therefore, if improved mixing efficiency is desired, a longer crystal must be used.

The measurement of the $\mathrm{sinc}^2(\Delta kl/2)$ signature for this crystal shows a phase-matching angle of 77° and a full base width of 12°±1°. This external angular base width compares well with the expected value of 12.5°. Measurements on a second 1-cm-long crystal verified its high quality.

These results show that CdSe has the required quality for the construction of an infrared parametric oscillator. The observed mixing efficiency of 35% corresponds to the same parametric gain.[1] For con-

TABLE I. Measured CdSe indices of refraction.

λ	n_0	n_e	$n_e - n_0$
1.0139	2.5481	2.5677	0.0196
1.1287	2.5246	2.5444	0.0198
1.3673	2.4971	2.5170	0.0199
1.5295	2.4861	2.5059	0.0198
1.7109	2.4776	2.4974	0.0198
2.3253	2.4627	2.4823	0.0196
3.00	2.4553	2.4748	0.0195
4.00	2.4500	2.4694	0.0194
5.00	2.4464	2.4657	0.0193
6.00	2.4434	2.4625	0.0191
7.00	2.4398	2.4586	0.0188
8.00	2.4367	2.4552	0.0185
9.00	2.4333	2.4514	0.0181
10.00	2.4294	2.4475	0.0181
11.00	2.4252	2.4430	0.0178
12.00	2.4204	2.4379	0.0175

struction of a collinear phase-matched single-resonant parametric oscillator with cw pumping, the single-pass signal gain must exceed the round-trip power loss or

$$\Gamma^2 l^2 > 2\alpha, \tag{6}$$

where α is the single-pass power loss. For a 1-cm crystal with $2\alpha = 0.1$, the required pump power density to reach threshold is $P/A = 1.0$ MW/cm^2.

In practice the parametric gain must exceed loss for a time duration long enough to allow the parametric fields to build up from the spontaneous noise. Typically this requires a net gain of 140 dB. For a 2-cm CdSe crystal pumped with a 10-MW/cm^2 power density in a 5-cm cavity, the buildup time is approximately 30 nsec, which is much less than the 200-nsec pump pulse length available at 1.833 μ. Under these conditions parametric oscillation should be obtained in CdSe with good conversion efficiency.

In conclusion, we have demonstrated the first phase-matched nonlinear interaction in CdSe and have verified the predicted infrared tuning curves. Using a Q-switched Nd : YAG laser operating at a 1.833-μ wavelength we have obtained a mixing efficiency of 35% at 2-kW input power. This corresponds to a 35% single-pass parametric gain and demonstrates that parametric oscillation is possible in CdSe. We have remeasured the nonlinear coefficient for CdSe and have verified previous measurements made relative to GaAs. Finally, we have proposed a CdSe infrared frequency converter pumped with wavelengths between 1.5 and 3 μ. The frequency converter can operate as a parametric oscillator with outputs between 2 and 4 μ and 8 and 12 μ or as a tunable infrared up-converter. A potential pump source is the LiNbO$_3$ parametric oscillator.

[†]Research supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by U. S. Army Research Office-Durham, Box CM, Duke Station, Durham, N. C. 27706, under Contract No. DAHC04-68-C-0048.

[1]S. E. Harris, Proc. IEEE 57, 2096 (1969).
[2]C. K. N. Patel, Phys. Rev. Letters 16, 613 (1966).
[3]G. D. Boyd, E. Buehler, and F. G. Storz, Appl. Phys. Letters 18, 301 (1971).
[4]W. L. Bond, J. Appl. Phys. 36, 1674 (1965).
[5]M. D. Martin and E. L. Thomas, IEEE J. Quantum Electron. QE-2, 196 (1966).
[6]Robert A. Bermeister, Ph. D. thesis (Stanford University, 1965) (unpublished).
[7]Ming-Pan Hung, Nobumistsu Ohashi, and Kenzo Igaki, Japan. J. Appl. Phys. 8, 652 (1969).
[8]J. H. McFee, G. D. Boyd, and P. H. Schmidt, Appl. Phys. Letters 17, 57 (1970).
[9]R. L. Byer, H. Kildal, and R. S. Feigelson, Appl. Phys. Letters 19, 237 (1971).
[10]W. B. Gandrud, Appl. Opt. 9, 1936 (1970).
[11]C. A. Klein and R. I. Rudko, Appl. Phys. Letters 13, 129 (1968).
[12]R. W. Wallace, J. Quantum Electron. QE-7, 203 (1971).
[13]R. L. Byer and S. E. Harris, Phys. Rev. 168, 1064 (1968).
[14]R. W. Wallace, Appl. Phys. Letters 17, 497 (1970).
[15]R. L. Byer, R. Feigelson, and J. F. Young, J. Appl. Phys. 41, 2320 (1970).
[16]C. C. Wang and C. W. Racette, Appl. Phys. Letters 6, 169 (1965).
[17]F. Zernike, Jr. and P. R. Berman, Phys. Rev. Letters 15, 999 (1965).
[18]W. L. Faust and C. H. Henry, Phys. Rev. Letters 17, 1265 (1966).
[19]G. D. Boyd and D. A. Kelinman, J. Appl. Phys. 39, 3597 (1968).

APPENDIX B

"SINGLY RESONANT CdSe INFRARED PARAMETRIC OSCILLATOR"

Appl. Phys. Letters (1 September 1972), to be published

SINGLY RESONANT CdSe INFRARED PARAMETRIC OSCILLATOR*

by

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ABSTRACT

We have demonstrated an infrared singly resonant parametric oscillator using CdSe as the nonlinear crystal. The oscillator operates with either a resonant signal near 2.2 μ or resonant idler in the 9.8 μ to 10.4 μ region. Using a Q-switched Nd:YAG laser operating at 1.833 μ as a pump source, we have observed thresholds of 550 W and up to 40% conversion efficiency. The angle tuned oscillator operates at room temperature with a 2 cm^{-1} bandwidth.

*Work supported in part by the United States Army Research Office-Durham under Contract #DAHC-04-68-C-0048 and the Office of Naval Research under Contract #N00014-67-A-0112-0070.

SINGLY RESONANT CdSe INFRARED PARAMETRIC OSCILLATOR

by

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We have recently demonstrated the high optical quality of CdSe and adequate nonlinear gain for efficient parametric conversion by a parametric mixing process.[1] Earlier, CdSe had been proposed as a possible nonlinear material for infrared parametric oscillators.[2] Using crystals of 1.8 cm and 2.1 cm lengths, we have obtained singly resonant oscillator (SRO) operation in the near and middle infrared at 2.2 μ and from 9.8 to 10.4 μ . Operation of the CdSe oscillator in the middle infrared has significantly increased the spectral coverage previously available with parametric oscillators.

CdSe has a wurzite structure with 6mm point group symmetry. It is positive birefringent. Only type II phasematching is allowed so that the energy and momentum conservation conditions are

$$\left.\begin{aligned} \omega_p &= \omega_s + \omega_i \\ \text{and} \\ n_p^o\omega_p &= n_s^e(\theta)\omega_s + n_i^o\omega_i \quad . \end{aligned}\right\} \qquad (1)$$

In the usual limit neglecting pump depletion, the parametric gain[2] coefficient is given by

$$\Gamma^2 \ell^2 = \frac{2\omega_s \omega_i d_{31}^2 P_p}{n_i n_s n_p (\epsilon_0 c)^3} \frac{\ell^2}{A} \quad , \qquad (2)$$

where $P_p = (\epsilon_0 n_p c/2)|E_p|^2 A_p$ and $A_p = \pi w_p^2/2$ for Gaussian beams. For the present SRO, the ratio of $\ell/b \sim 0.16$, where $b = w^2 k = w^2 \omega n/c$. The optimum focusing condition for a doubly resonant oseillator[3] is assumed to hold for the SRO ease so that $b_p = b_s = b_i$ and $A = (\pi/2)(w_s^2 + w_i^2)$.

For the present 2.1 em CdSe erystal with the above focusing, the single pass gain is $\Gamma^2 \ell^2 = 1.85 \times 10^{-4} P_p$. Here we have used the measured value of $d_{31} = 2.5 \times 10^{-22}$ mks from Ref. 1. Setting the calculated gain equal to a round trip eavity loss of approximately 10% which is primarily due to the distributed erystal loss, we caleulate a threshold of 540 W . The measured threshold of 550-770 W is in good agreement with the theoretieal value.

Figure 1 shows a sehematie of the present experiment. We use a Q-switched Nd:YAG laser operating at 1.833 μ as a pump source.[4] The laser operates at room temperature with up to 5 kW peak output power in a 300 nsee pulse at typieally 5 pps . The 1.833 μ source is not visible on an infrared image eard so we use a eollinear 1.15 μ HeNe laser as an alignment aid. The oseillator operates with a near confocal cavity with fused siliea mirrors of 5.7 cm radius that are high reflecting at the signal. To insure singly resonant operation, a

Brewster angle fused silica plate is inserted in the cavity with negligible loss at the resonant signal wave. The plate simultaneously acts as an output coupler for the orthogonally polarized 9.8 μ idler wave which is detected by a pyroelectric detector.[5] A fast InSb detector monitors the signal wave. A silicon diode preceeded by an angle phasematched $LiIO_3$ doubling crystal detects the transmitted pump wave. We have measured power conversion efficiencies of up to 40% by monitoring depletion of the transmitted pump wave.

Figure 2(a) shows the complete angle tuning curve for CdSe calculated from index of refraction data.[1] Also shown is the calculated gain bandwidth

$$BW(cm^{-1}) = \frac{1}{\ell c}\left(\frac{\partial k_s}{\partial \omega_s} - \frac{\partial k_i}{\partial \omega_i}\right)^{-1} . \qquad (4)$$

Figure 2(b) shows the measured output wavelength as a function of propagation direction with respect to the optic axis. The solid line is the theoretical tuning curve. We tune the oscillator by rotating the CdSe crystal about its front surface and simultaneously translating the cavity mirror to compensate for beam translation. The geometric aperture of the crystal limits the tuning angle to a maximum of 78°. The threshold increases during tuning by $\cos^2\theta$ due to the decrease in the effective d_{31}^2. The entire tuning range from 9.8 to 15 μ may be covered by a single crystal if cut at a 75° propagation direction. The aperture length at a 75° propagation direction for the present focusing is $\ell_a = \sqrt{\pi}\, w_s/\rho = 6.3$ cm where ρ is the double refraction angle.

This is longer than the crystal length so that walkoff is not a problem. It should be mentioned that CdSe does not have enough birefringence to phasematch over the middle infrared region from 4 to 8 μ. The pump wavelength that gives the widest tuning range from 3.3 to 4.0 μ and 8.0 to 15 μ is 2.7 μ, which is near the intense HF laser lines.[6]

We have measured an oscillator bandwidth of 2.0 cm^{-1} at 2.25 μ using a 3/4 meter Spex spectrometer. This is less than the calculated gain bandwidth of 9 cm^{-1} and is probably due to operation near threshold. We expect to reduce the oscillator linewidth significantly by use of an intracavity etalon as has been previously reported.[7,8,9]

Crystal surface damage limits the operation of the oscillator to less than two times above threshold. This leads to insufficient gain to assure good pulse to pulse oscillator stability. The observed surface damage occurs on both the front and back surfaces of the CdSe crystal and is due to the resonant signal wave. An estimate of the circulating signal power for the resonant signal is seven to eight times the incident pump power when the oscillator is 2.4 above threshold.[10] This gives a signal power density at the crystal surface near the measured crystal burn density of 30 MW/cm^2 assuming a Gaussian beam area of πw_s^2.[(1)] This burn density corresponds to the 60 MW/cm^2 reported by Smith et al.[11] for an effective area of $\pi w_s^2/2$.

We note that by resonating the idler the circulating cavity power is reduced by the photon energy ratio ω_s/ω_i. In addition, the idler power density is reduced by the area factor $\pi w_i^2/\pi w_s^2 = \omega_s/\omega_i$. In our

case for operation far from degeneracy, this factor is $(4.5)^2$.

We resonated the idler wave using 5 cm radius GaAs mirrors with ~~90% reflectivity~~ at 9.8 μ . Due to the increased coating and crystal losses the threshold was greater than the power available from the pump laser. To decrease threshold we replaced the second GaAs mirror by a gold coated mirror which reflected the pump, signal, and idler waves. This round trip cavity reduced the threshold to a measured level of 2.33 kW for a round trip loss near 40%. At two times above threshold the resonated idler power inside the cavity was only 0.4 P_p which gave a power density below the crystal burn density. The oscillator operated without surface damage due to the resonant idler wave. However, the GaAs-gold mirror cavity acted to partially resonate the pump wave. The enhanced pump field inside the resonator did damage the thorium fluoride antireflection coatings but not the crystal surface. As expected, the damage was independent of the oscillator operation.

CdSe is a high quality nonlinear optical material which does not show birefringence variations or index inhomogeneities due to intense laser fields. Its intensity damage threshold of 30 MW/cm^2 gives a maximum $\Gamma^2\ell^2 = 2.94$ for a 1.833 μ pump and 2.0 cm crystal. At this time crystals up to 3 cm are commercially available[1] with longer, higher quality crystals having been reported.[12] We expect that tunable output should be available from CdSe singly resonant oscillators in the 2 to 4 μ and 8 to 15 μ regions without crystal burning problems for crystal lengths of 4 cm. Crystals of this length have one third the gain of 4 cm $LiNbO_3$ crystals and should operate as reliably in the

SRO configuration.

In conclusion, we have demonstrated a new tunable infrared source which operates at room temperature and is conveniently tuned by crystal rotation. The CdSe singly resonant oscillator significantly extends the spectral range available from existing parametric oscillators. It promises to be a useful and convenient noncryogenic source of tunable coherent radiation in the middle infrared.

REFERENCES

1. R. L. Herbst and R. L. Byer, "Efficient Parametric Mixing in CdSe," Appl. Phys. Letters 19, 527 (1971).
2. S. E. Harris, "Tunable Optical Parametric Oscillators," Proc. IEEE 57, 2096 (1969).
3. G. D. Boyd and D. A. Kleinman, "Parametric Interaction of Focused Gaussian Light Beams," J. Appl. Phys. 39, 3597 (1968).
4. R. W. Wallace, "Oscillation of the 1.833 μ Line in Nd^{3+}:YAG," IEEE J. Quant. Elec. QE-7, 203 (1971).
5. R. L. Byer and C. B. Roundy, "Pyroelectric Coefficient Direct Measurement Technique and Application to a nsec Response Time Detector," Ferroelectrics 3, 333 (1972).
6. O. R. Wood and T. Y. Chang, "Transverse-Discharge Hydrogen Halide Lasers," Appl. Phys. Letters 20, 77 (1972).
7. L. B. Kreuzer, "Single Mode Oscillation of a Pulsed Singly Resonant Optical Parametric Oscillator," Appl. Phys. Letters 15, 263 (1969).
8. J. Pinard and J. F. Young, "Interferometric Stabilization of an Optical Parametric Oscillator," Optics Communications 4, 425 (1972).
9. R. W. Wallace, private communication.
10. Paul P. Bey and Chung L. Tang, "Plane-Wave Theory of Parametric Oscillator and Coupled Oscillator-Upconverter," IEEE J. Quant. Elec. QE-8, 361 (1972).
11. D. C. Hanna, B. Luther-Davies, H. N. Rutt, R. C. Smith, and C. R. Stanley, "Q-Switched Laser Damage of Infrared Nonlinear

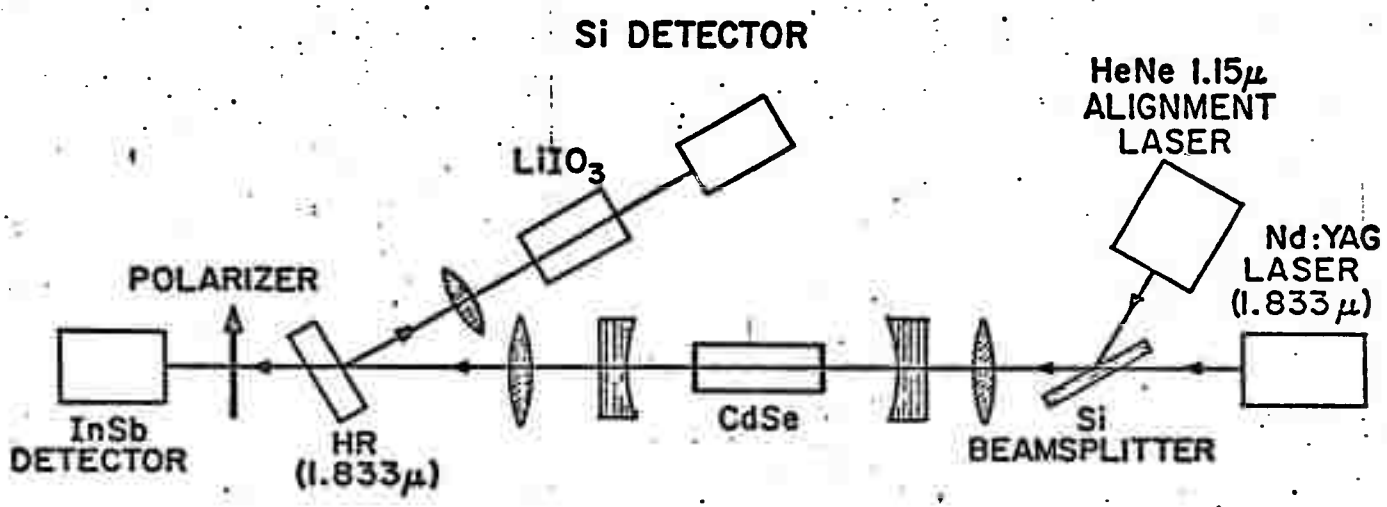
Materials," IEEE J. Quant. Elec. QE-8, 317 (1972).

12. S. A. Abagyan, G. A. Ivanov, A. A. Kartushina, and G. A. Koroleva, "Spectral Dependence of Birefringence of CdSe," Sov. Phys. — Semicond. 5, 1425 (1972).

FIGURE CAPTIONS

Figure 1 Schematic of single resonant CdSe infrared parametric oscillator.

Figure 2 (a) Angle tuning curve for CdSe for a 1.833 μ pump.
(b) Experimental tuning data (points) and theoretical curve (line).



CdSe INFRARED PARAMETRIC OSCILLATOR

Figure 1

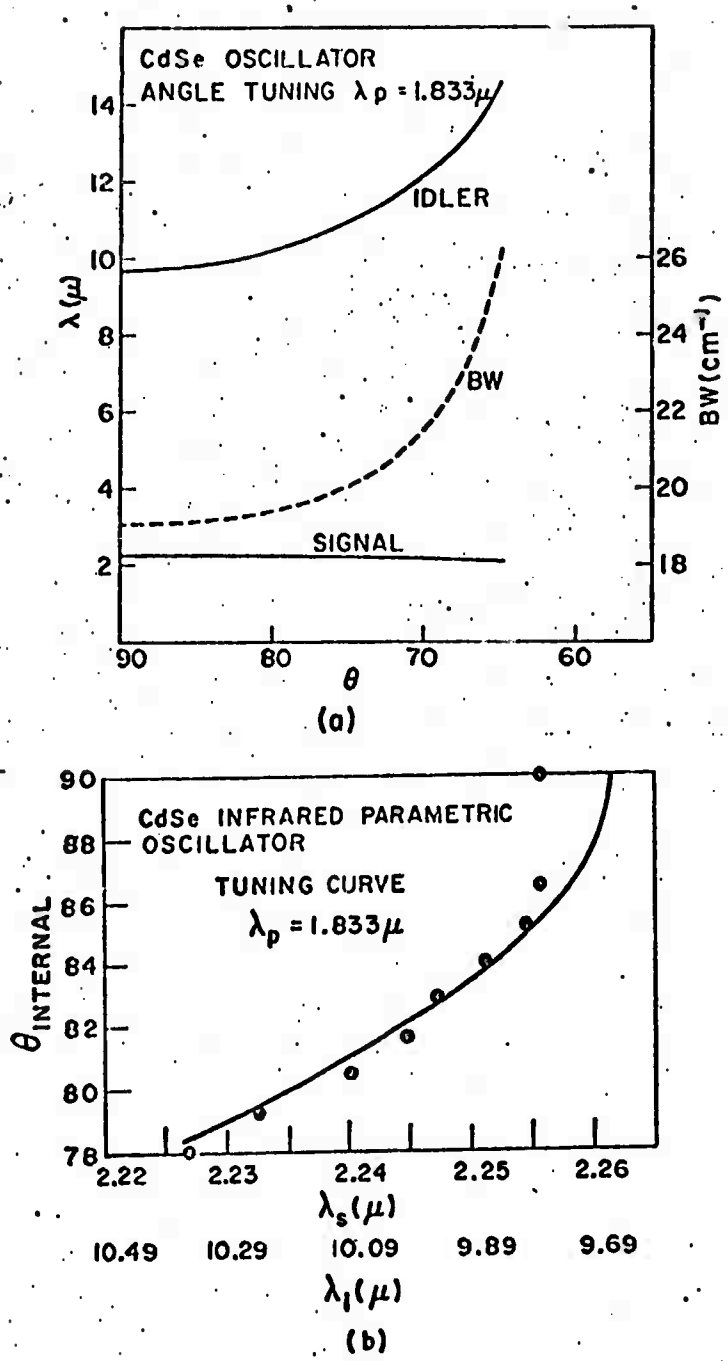

CdSe OSCILLATOR
ANGLE TUNING λp = 1.833μ
IDLER
BW
SIGNAL
λ(μ)
BW(cm⁻¹)
θ
(a)
CdSe INFRARED PARAMETRIC OSCILLATOR
TUNING CURVE
λp = 1.833μ
θINTERNAL
λs(μ)
λi(μ)
(b)

Figure 2

APPENDIX C

"OPTICALLY PUMPED MOLECULAR IODINE VAPOR-PHASE LASER"

Appl. Phys. Letters, 20, (June 1972)

Optically Pumped Molecular Iodine Vapor-Phase Laser*

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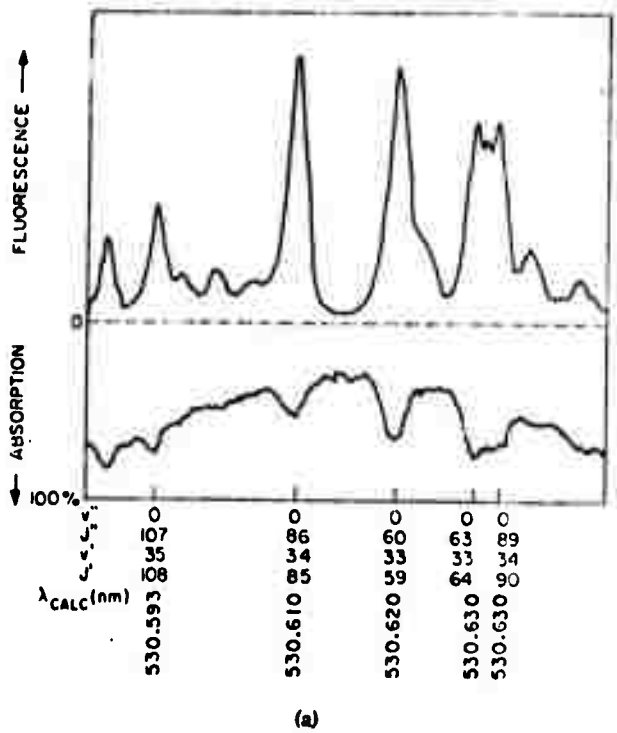
We have observed stimulated emission in optically pumped molecular iodine vapor. Laser action occurs in more than 150 individual lines which span the spectral region from 544 to 1.335 nm for excitation by the 530-nm second-harmonic wavelength of a Q-switched Nd:YAG laser. The iodine laser oscillates for input pulse energies of a few microjoules. Approximately 10^6 individual laser transitions may be excited by various pump frequencies.

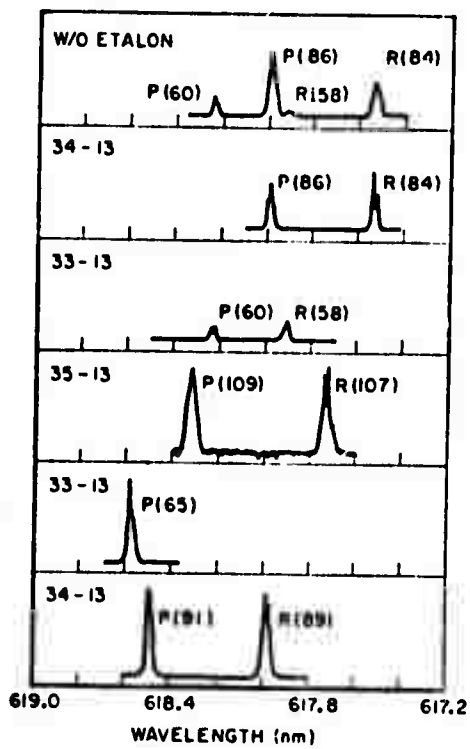
We have observed stimulated emission in optically pumped molecular iodine vapor. A Q-switched Nd:YAG laser operating at various second-harmonic wavelengths pumps selected vibrational-rotational levels of the $B^3\Pi_{0u}^+ - X^1\Sigma_g^+$ electronic transition.[1] This leads to population inversion between the excited B state and the higher vibrational levels of the X state, yielding a series of molecular laser transitions from 544 to 1.335 nm.

Pumping an 8-cm Brewster-angle cell at room temperature, we have obtained peak output powers of 1 W in a single line (618 nm) at 0.5% conversion efficiency. We used a 5.5% transmitting output mirror and a Brewster-angle quartz prism to select individual lines. For the present 190-nsec pump pulse, each iodine molecule is used once, and the maximum output power is limited by the number of iodine molecules. For the 8-cm cell and a 19.5-cm cavity, the laser threshold is as low as a few microjoules of pump energy.

Recently, stimulated emission across the far infrared has been generated by optically pumping methyl fluoride, ammonia, and other molecules at 10.6 μ.[2] Sorokin and Lankard[3] have optically pumped molecular cesium, rubidium, and potassium by two-photon absorption followed by dissociation into excited atomic states, producing stimulated emission between the atomic transitions. Laser action has not been previously reported in molecular iodine. Atomic iodine, however, has been reported to lase in a few infrared lines when pumped by a pulsed high-voltage electrical discharge[4] or by photo-



(a)



(b)

FIG. 1. (a) High-resolution absorption and fluorescence spectra of I_2 centered at 530.6 nm, the second-harmonic output of a Nd:YAG laser. The spectra were taken by tilting a 2.5-mm sapphire etalon within the Nd:YAG cavity. The vibrational-rotational numbers of the principal I_2 absorption lines are indicated with their calculated wavelengths in air. (b) Resolved output of the I_2 laser at the 618-nm wavelength region. See Table II for wavelength values.

dissociation.[5-7] Except for organic dye lasers which tune continuously over a limited region of the spectrum, most lasers show stimulated emission at a few discrete wavelengths. Molecular iodine is an intermediate case with potentially 10^4 discrete laser transitions distributed through the visible and near infrared region. We observe laser action to approximately every second vibrational level of the ground state from $v'' = 2$ to $v'' = 73$. The largest v'' is determined by the pump wavelength and the right-hand turning point of the B state. The missing vibrational transitions are due to unfavorable Franck-Condon factors.[8,9] Each transition is a doublet composed of the R and P transitions separated by a few angstroms.

We have pumped the iodine laser with the second-harmonic output of three Nd:YAG laser lines at 530.6, 532.0, and 536.7 nm. Table I is a partial list of iodine laser wavelengths observed to date. Since the iodine absorption spectrum is very dense near 530 nm with more than ten strong lines per angstrom, the pump laser with a linewidth of 0.2 Å pumps more than one transition. The main lines of the iodine laser output therefore consist of two separate doublets, and the listed iodine laser wavelengths are an average.

To allow selective excitation of single vibrational-rotational levels, we inserted a 2.5-mm-thick sapphire etalon into the Nd:YAG laser cavity. This simplifies wavelength assignments and permits accurate determination of iodine laser parameters. The etalong narrowed the bandwidth of the pump laser from 0.8 to 0.1 cm^{-1}, and by tilting the etalon the laser output could be turned over more than 2.0 cm^{-1} to selectively pump five separate iodine transitions. Figure 1(a) shows the recorded high-resolution absorption and fluorescence spectrum of iodine at 530.6 nm. The iodine laser oscillates when pumped at each of the indicated absorption lines. Figure 1(b) shows the resulting iodine laser output at 618 nm taken with a $\frac{3}{4}$-m Spex spectrometer. The first spectrum, without the etalon in the Nd:YAG laser cavity, shows two doublets. Using the etalon, these are resolved as shown in the next two spectra. In addition, the increased pump tuning range due to the etalon allows pumping of three new transitions shown by the last three spectra. The full vibrational-rotational assignment is determined by comparing the experimental wavelengths with the calculated wavelengths using the molecular constants of Steinfeld *et al.*[9] and LeRoy.[10]

TABLE I. Partial list of observed I_2 molecular laser wavelengths.

Pump wavelength (nm)	Iodine laser wavelengths (nm)					
530.6	555.0	574.5	588.0	617.5	649.0	LMR[a]
	568.0	581.5	602.5	633.0	664.5	
531.9	544.3	651.1	906.0	1005.3	1107.3	1329.1
	556.7	659.2	928.8	1022.5	1125.5	1331.0
	569.7	676.3	929.5	1024.5	1135.0	1332.4
	576.4	693.6	930.5	1025.5	1287.0	1333.3
	590.5	711.4	954.5	1053.4	1292.5	1334.9
	604.8	LMR[a]	955.5	1077.5	1315.3	
	619.8	881.3	996.3	1078.8	1319.2	
	635.2	904.7	997.3	1106.6	1328.2	

[a] Limited by mirror reflectance.

TABLE II. Comparison of measured and calculated wavelengths in air for the I$_2$ laser.

Transition $v' \rightarrow v''$	λ_{meas} (nm)	λ_{calc} (nm)	Difference
35→13 *R*(107)	617.730	617.676	0.054
P(109)	618.325	618.267	0.058
34→13 *R*(89)	617.970	617.947	0.023
P(91)	618.490	618.441	0.049
34→13 *R*(84)	617.520	617.482	0.038
P(86)	617.990	617.947	0.043
33→13 *R*(58)	617.900	617.868	0.032
P(60)	618.245	618.193	0.052
33→13 *P*(65)	618.580	618.535	0.045

As an example, Table II lists the calculated and measured wavelengths for the 618-nm laser transition for a 530.6-nm pump. The measured wavelengths were taken with the $\frac{3}{4}$-m Spex calibrated against mercury lines and the 632.8-nm HeNe line. The 0.5-Å offset in calculated and measured wavelength is probably due to the offset error in the spectrometer. The wavelength and rotational splitting agreements confirm the spectral assignments.

In addition to the Brewster prism, a 1-cm fused silica etalon was inserted into the iodine laser cavity. The gain linewidth measured by tilting the etalon was 1.5 GHz, which is larger than predicted by Doppler broadening. This is due to the expected hyperfine splitting of $^{127}I_2$,[11,12] which has either 15 or 21 hyperfine components. The total hyperfine splitting is almost 1 GHz which added to a room-temperature Doppler full width of 380 MHz at 618 nm gives a reasonable agreement with the measured value.

We have solved the rate equations for the iodine system and have derived expressions for the gain and saturation output power. The total lifetime t_2 of the excited B state depends on the spontaneous decay time t_0 and the collisional quenching time t_q with $1/t_2 = 1/t_0 + 1/t_q$. The spontaneous decay time includes both fluorescence decay to the ground state and also spontaneous decay into an unbounded iodine state that dissociates. Recent estimates suggest that at low pressures approximately 30% of the excited I_2 molecules decay by dissociation.[13] Since these do not contribute to the lasing action, this reduces the over-all conversion efficiency. The collisional quenching time depends on the iodine pressure. We operated the cell at room temperature (25 °C), which corresponded to an iodine pressure of 0.32 Torr.[14] From Chutjian *et al.*[15] we estimate $t_0 = 900$ nsec and $t_q = 191$ nsec to give $t_2 = 157$ nsec. The rotational and vibrational relaxation times are much longer such that during the 190-nsec pump pulse there is negligible cross coupling between the rotation-vibrational levels within the X and B states.

We determine the gain of a single line by measuring the time delay between the pump pulse and the onset of laser oscillation, taking as the threshold the time t_b when the laser power inside the cavity has built up to 0.2 W. This power level corresponds to 4×10^8 photons in the cavity. Since the laser builds up from one spontaneously emitted photon, we can write the threshold condition as

$$\frac{c}{L}\int_{t_a}^{t_b}\left[g\left(\frac{N_2 - (d_2/d_1)N_1}{N_1^0/2}\right) - \alpha\right]dt \approx 20, \qquad (1)$$

where g is the single pass gain, α is the single pass loss, and L is the cavity length. $N_2 - (d_2/d_1)N_1$ is the population inversion of the laser transition, with N_2 and N_1 the upper and lower laser level populations, respectively, and d_2 and d_1 the degeneracy factors. N_1^0 is the equilibrium molecular density of the rotational-vibrational ground-state level being pumped. The integration is from the time t_a, the time when the gain first surpasses the loss, until the time the laser power in the cavity reaches the defined threshold.

Below threshold $N_2 \approx 0$, and for large pump powers such that the pump transition is rapidly saturated, $t_a \approx 0$. Since the ground-state thermalization time is much longer than the laser pump pulse and the upper-state decay time, we can derive a simplified expression for the gain calculated from the laser buildup time,

$$g = \frac{\alpha + 2\alpha L/ct_b}{(2t_2/t_b)[1 - \exp(-t_b/2t_2)]}, \qquad (2)$$

when the degeneracy factor $d_1 \approx d_2$. Table III lists the measured single pass gain for the 8-cm iodine cell. The single pass loss including scattering, absorption, and output coupling is 5%, and we use $t_2 = 157$ nsec.

The theoretical expression for gain based on iodine molecular parameters is

$$g = \left(\frac{1}{4\pi\epsilon_0 c\hbar}\right)\left(\frac{4\pi^2\nu}{3}\right)|R_e|^2 q_{v',v''}\frac{S_{J''}}{2J''+1}f(\nu - \nu_0)N_{v'',J''}l, \qquad (3)$$

where ν is the frequency, $|R_e|^2 = 1.03D^2$,[12] $q_{v',v''}$ is the Franck-Condon factor, $S_{J''}$ is the rotational line strength, $f(\nu - \nu_0)$ is the lineshape function, and l is the cell length. We consider the 33-13 $P(65)$ transition where $N_{v'',J''} = \frac{1}{2}N_{0,63}$, which is half the ground-state population. For the present iodine cell $N_{0,62} = 7.3 \times 10^{12}$ cm^{-3}. From Steinfeld *et al.*[9] $q_{33,13}$ is approximately 0.01. The lineshape function is $f(0) = (2/\Delta\nu_0)(\ln 2/\pi)^{1/2}$ with the linewidth $\Delta\nu_0 = 1.5$ GHz. With the above parameters the calculated gain is $g = 19\%$ for an 8-cm cell. This agrees well with the measured value. The Franck-Condon factors are such that we should expect approximately the same gain for all strong laser transitions.

The maximum output energy per pulse is limited by the total number of molecules $N_{0,J''}$ in the rotational-vibrational ground-state level. With V equal to the mode volume, the maximum energy in a doublet is $E_{max} = \frac{1}{2}\hbar\omega N_{0,J''}V$. For mode matching into an 8-cm cell in a 14.5-cm cavity and $J'' = 63$, we calculate $E_{max} = 0.10$ μJ for the laser output at 618 nm. The measured maximum output energy is 0.054 μJ. The difference is mainly due to the upper-state losses during the buildup period.

TABLE III. Single-pass gain in an 8-cm I_2 cell at 25 °C for a $v' = 33$ to $v'' = 13$ laser transition.

L (cm)	t_b (nsec)	g (%)
14.5	80	19±3
24	150	20±3

In conclusion, we have demonstrated an optically pumped molecular iodine laser with a multitude of lines over an extended frequency range. Besides its unique properties, the laser can provide insight into the spectroscopy of iodine. For example, accurate wavelength measurements can now be extended to the dissociation limit. In addition, the gain measurement technique described in this paper leads to a direct measurement of Franck-Condon overlap factors.

The authors wish to acknowledge helpful discussions with Professor A.L. Schawlow.

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*Research sponsored in part by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract No. F44620-71-C-0053, and the National Science Foundation under Grant No. GP-28415.

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[1]Robert S. Mulliken, J. Chem. Phys. 55, 288 (1971).

[2]T.Y. Chang and J.D. McGee, Appl. Phys. Letters 19, 103 (1971).

[3]P.P. Sorokin and J.R. Lankard, J. Chem. Phys. 54, 2184 (1971).

[4]G.R. Fowles and R.C. Jensen, Proc. IEEE 52, 851 (1964); Appl. Opt. 3, 1191 (1964); Proc. IEEE 52, 1350 (1964).

[5]Jerome V.V. Kasper and George C. Pimentel, Appl. Phys. Letters 5, 231 (1964).

[6]V. Yu Zalesskii and A.A. Venediktov, Sov. Phys. JETP 28, 1104 (1969).

[7]D.E. O'Brien and J.R. Bowen, J. Appl. Phys. 40, 4767 (1969).

[8]R.N. Zare, J. Chem. Phys. 40, 1934 (1964).

[9]J.I. Steinfeld, R.N. Zare, L. Jones, M. Lesk, and W. Klemperer, J. Chem. Phys. 42, 25 (1965).

[10]Robert J. LeRoy, J. Chem. Phys. 52, 2683 (1970).

[11]G.R. Hanes and C.E. Dahlstrom, Appl. Phys. Letters 14, 362 (1969).

[12]T.W. Hänsch, M.D. Levenson, and A.L. Schawlow, Phys. Rev. Letters 26, 946 (1971).

[13]A. Chutjian and T.C. Jaines, J. Chem. Phys. 51, 1242 (1969).

[14]Andrei Nikolaevich Nemetanov, *Vapor Pressure of the Elements* (Academic, New York, 1963).

[15]A. Chutjian, J.K. Link, and L. Brewer, J. Chem. Phys. 46, 2666 (1967).